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Optimizing catalysts for solar fuel production: Spectroscopic  
characterization of the key reaction intermediates

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**Final Report**

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<b>14. ABSTRACT</b> The purpose of this grant was to develop a new and general way to isolate key reaction intermediates in the condensed phase catalytic conversion of carbon dioxide and water into transportable solar fuels. To this end, we designed, constructed and implemented a chemical analysis apparatus to extract homogeneous catalysts from their native solution environment and isolate them for spectroscopic study. This was achieved using an electrospray atmospheric pressure interface to a custom built, multi-stage, cryogenically cooled photofragmentation mass spectrometer. The key advance incorporates a 10K processing stage, which freezes ions into well defined structures and coats them with an inert layer of weakly bound adducts. These cold aggregates were then complexed with target molecules to initiate chemical rearrangements under conditions where the reactions could be arrested prior to completion by rapid evaporation of the cryogenic solvent.					
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# **AFOSR Final Performance Report**

**FA9550-09-1-0139**

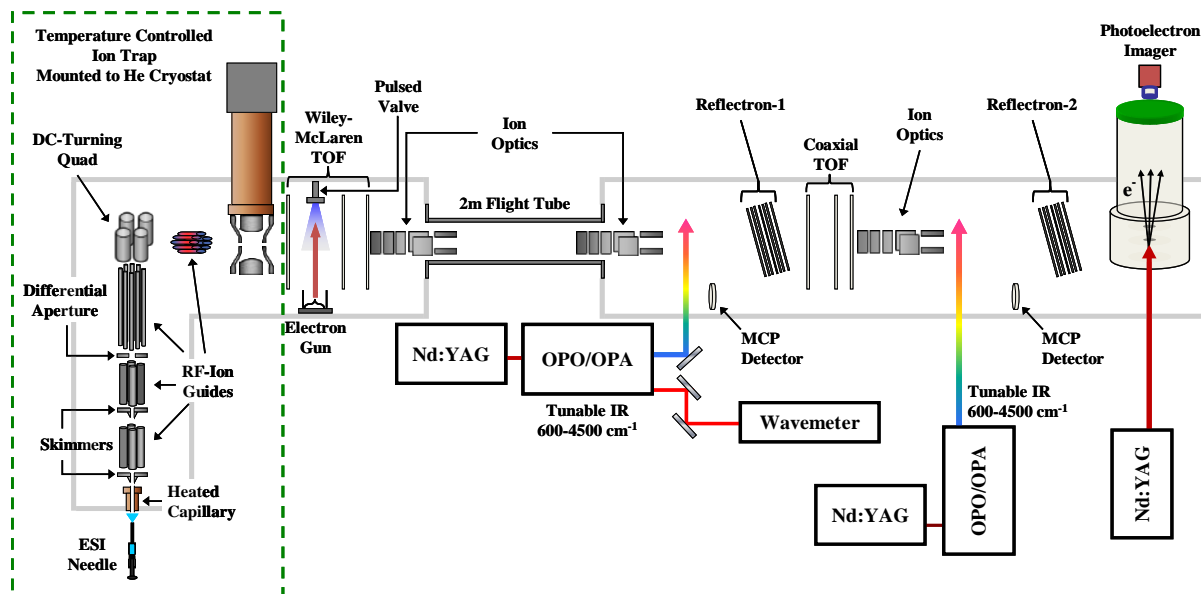
## **Optimizing catalysts for solar fuel production: Spectroscopic characterization of the key reaction intermediates**

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New Haven, CT  
28 February 2013

The long-standing focus of our program is to provide precision measurements of the structures of reactive species that are invoked to explain macroscopic behavior, but have proven impossible to obtain using traditional methods of chemical analysis. The specific goal of the work carried out under this grant was to develop a new and general way to isolate key reaction intermediates in the condensed phase catalytic conversion of carbon dioxide and water into transportable solar fuels. Because such measurements cannot be obtained with commercially available analytical instruments, we designed, constructed and implemented a chemical analysis apparatus specifically created to capture and structurally characterize transient species central to chemical processes relevant to AFOSR goals. The scheme is based on extraction of homogeneous catalysts from their native solution environment and isolating them free from solvent using an electrospray atmospheric pressure interface to a custom built, multi-stage, cryogenically cooled photofragmentation mass spectrometer. The key advance incorporated into this instrument is the introduction of a cryogenic (10K) ion processing stage, where ions can be frozen into well defined structures and coated with an inert layer of weakly bound adducts (typically Ar, H<sub>2</sub>, or N<sub>2</sub>). These aggregates are then complexed with CO<sub>2</sub> or H<sub>2</sub>O to initiate chemical rearrangements under conditions where the reactions can be arrested prior to completion by rapid evaporation of the cryogenic solvent. Thus captured, the structures of the intermediates are determined by theoretical analysis of their vibrational spectra, obtained in an isomer-selective manner using multi-step infrared laser excitation. After demonstrating the capabilities of this approach to unravel intermediates in catalytic transformation of nitrosonium into nitrous acid, a key reaction in the ionosphere, we obtained the structures of critical intermediates in the pyridine-based photoelectrocatalytic reduction of CO<sub>2</sub> as well as several oxidation catalysts based on Ir, Mn and Ni organometallic compounds.

## I. EXPERIMENTAL APPROACH

The basic layout of the instrument used in our AFOSR work is shown in Fig. 1. This instrument consists of a versatile set of ion sources that deliver species of interest into three laser interaction regions and three stages of mass selection. This configuration allows routine determination of isomer-selective vibrational (and, for negative ions photoelectron) spectra of species cooled and “tagged” with weakly bound mass “messengers” (e.g., Ar, H<sub>2</sub>, N<sub>2</sub>, etc.). Such tagging serves two purposes: first it ensures the target species are cold and second, it enables acquisition of spectra in a *linear* action mode (i.e., where photofragments are monitored as a function of excitation frequency.) The latter feature is crucial because it allows the use of rather low power table top lasers throughout the IR, and also yields spectra that are directly related to calculated absorption spectra. During the course of the previous grant, we dramatically broadened the scope of chemical systems that can be studied by implementing atmospheric ionization (e.g., electrospray) in conjunction with cryogenic ion processing to allow the action spectroscopy methods to be applied to species extracted directly from solution. That component of the instrument is shown on the left of Fig. 1, and is interfaced directly to the powerful optical



**Fig. 1.** Schematic of the custom-built Yale triple-focusing mass spectrometer, a versatile spectroscopic platform for structural characterization of cold, isomer-selected gas phase ions. The atmospheric ionization source (green box) was added during the course of the previous grant.

spectrometric capabilities developed to study Ar-solvated ions initially created in the free jet. In addition to this instrument, however, we have also commissioned a new lab in the spring of 2011 which features a 7T superconducting ion cyclotron resonance spectrometer (ICR) which has much higher ( $\sim 100\times$ ) mass resolution.

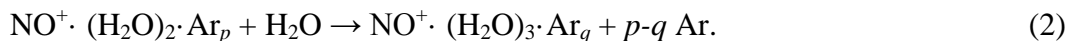
## II. RESULTS

### IIA. Water cluster-mediated conversion of $\text{NO}^+$ to HONO in the ionosphere: Network dependence of proton coupled covalent bond formation

An interesting aspect of ion chemistry in Earth's atmosphere comes from the field observation (by an Air Force rocket-based probe) that cations in the D-region of the ionosphere primarily occur as protonated water clusters, in spite of the fact that the direct ionization mechanisms create ions derived from the abundant nitrogen and oxygen molecules. This phenomenon has been rationalized by a water cluster-mediated scheme in which nitrosonium,  $\text{NO}^+$ , is converted to nitrous acid, HONO, and protonated water upon the addition of the fourth water molecule to the growing hydration shell:



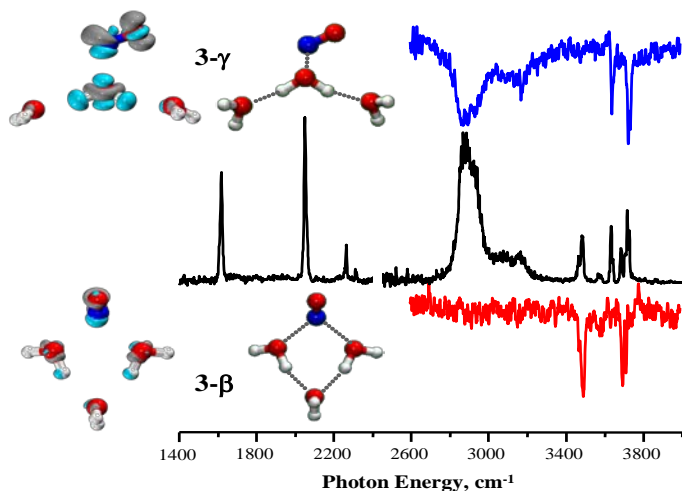
This reaction involves the chemical activation of a water molecule by charge translocation from the  $\text{NO}^+$  solute ion onto the water network with concomitant N-O bond formation. Our interest in this system was first to demonstrate the capabilities of the new instrument, and second to explore some motifs that are closely related to those at play in the chemical transformation of water molecules in biomimetic water splitting for the storage of solar energy. Specifically, critical steps in both are O-O bond formation in photosynthetic water oxidation and N-O bond formation in HONO production, which in each case involves removal of the H atoms by proton transfer and concomitant charge translocation to the surrounding medium. For decades, it had been speculated that the water-mediated  $\text{NO}^+$  conversion to HONO must involve unusual configurations of the water network, and we set out, at the request of Albert Viggiano at AFRL (then at Hanscom), to reveal the operative solvent configurations using cryogenic ion chemistry to trap metastable configurations of the trihydrate:



This work effectively leveraged our long-standing efforts to understand the behavior of water networks in the immediate vicinity of an ion.

The key to understanding the  $\text{NO}^+(\text{H}_2\text{O})_n$  system was the implementation of isomer-selective IR-IR hole burning spectroscopy. This technique, developed in our lab under AFOSR support, uses two lasers and three stages of mass selection to isolate the vibrational signature of a particular isomer. In this case, we recovered three isomeric structures for the critical  $\text{NO}^+(\text{H}_2\text{O})_3$  cluster that displayed drastically different degrees of chemical activity. Theoretical analysis (provided by Profs. Anne McCoy (The Ohio State U.), Ken Jordan (U. of Pittsburg) and Ryan Steele (now at U. of Utah)) of the isomeric structures revealed the extent of charge transfer and heavy atom bond formation. This can be readily seen in the electron density difference plots shown in Figure 2, where the 3- $\gamma$  (spectrum in blue) isomer indeed shows the largest degree of N-O bond formation. Our analysis provides an explicit, molecular-level description of the “solvent coordinate,” ubiquitous in the discussion of aqueous chemical reactions and is an important step toward understanding how network geometries control water activation and heavy atom bond formation. This work [ref. (3)] was reported as an article in *Science* and appeared along with a Perspective (<http://www.sciencemag.org/-/content/327/5963/280.short>) in addition to being highlighted by the editors of *Nature Chemistry* (<http://dx.doi.org/10.1038/nchem.578>).

In a follow-up paper, we combined theoretical analysis (this time with Jürgen Troe),

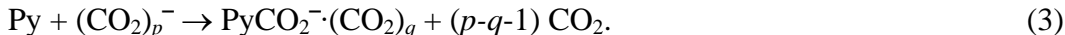


**Fig. 2.** Isomer-specific IR-IR hole burning spectra (colored) revealing two of the three  $\text{NO}^+(\text{H}_2\text{O})_3$  isomers present in the vibrational predissociation spectrum (black). The reactive isomer (blue) is clearly evident by the strongly red-shifted bands in the upper trace, where two water molecules in the second solvation shell promote proton transfer and concomitant N-O covalent bond formation.

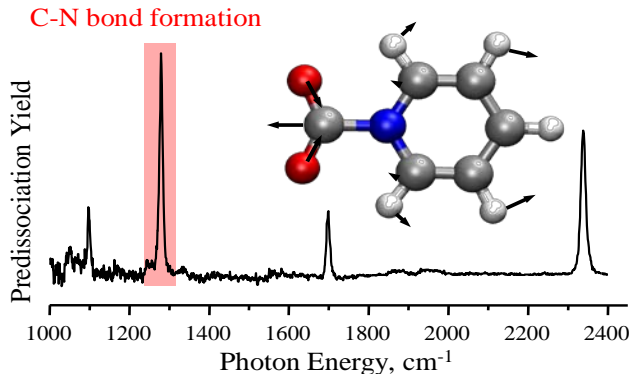
temperature-dependent kinetics (AFRL), and photoactivation (Yale) of the trapped  $\text{NO}^+(\text{H}_2\text{O})_{3,4}$  complexes to assess whether these isomers were persistent (and thus relevant) at the ambient conditions in the ionosphere. Critical analysis indicates that the barriers to interconversion are likely too small to support the metastable isomers playing the role of distinct reaction pathways, but more likely these metastable configurations are sampled in the course of most bimolecular encounters.

## IIB. Isolation of the carbamate free radical anion invoked in the mechanism for photo-electrochemical activation and conversion of CO<sub>2</sub> to methanol

Our long standing expertise on the properties of CO<sub>2</sub> clusters enabled a very effective first venture into issues central to CO<sub>2</sub> activation. Because activation schemes often involve electrochemical reduction, it is critical that at least partially bent CO<sub>2</sub> moieties be accessible (recall that the CO<sub>2</sub> anion, like isoelectronic NO<sub>2</sub>, is bent). A very exciting development in this regard is Bocarsly’s recent report of pyridine-catalyzed photoelectroreduction of CO<sub>2</sub> to methanol (and other value-added products like formaldehyde and formate). We demonstrated a powerful way to access the radical anion intermediates by reaction of key species with gas phase (CO<sub>2</sub>)<sub>n</sub><sup>−</sup> clusters, which are readily generated in ionized free jet ion sources. The carbamate anion radical was thus obtained by condensation of pyridine (Py) onto the CO<sub>2</sub> clusters:



The propensity of this system to undergo chemical reaction is of particular interest in light of recent work suggesting that the formation of a carbamate between Py and CO<sub>2</sub> is the rate-limiting step in the overall reduction to methanol. Theoretical analysis has found the formation of a carbamate to be energetically unfavorable unless either the Py or CO<sub>2</sub> begins as an anion. The CO<sub>2</sub>-Py radical anion is reminiscent of the CO<sub>2</sub> adduct to a nitrogen base isolated as a zwitterion by Villiers and coworkers, where the C-N stretch was observed at 1605 cm<sup>−1</sup>. The results of our vibrational characterization of the Py(CO<sub>2</sub>)<sup>−</sup> clusters are summarized in Fig. 3 and published in ref. [4]. We determined that the C-N stretch in the Py(CO<sub>2</sub>)<sup>−</sup> ion occurs at ~1270 cm<sup>−1</sup>, considerably lower than that found in the zwitterions. This behavior is consistent with the idea that Py attachment provides an excellent CO<sub>2</sub> reduction catalyst because its adduct is quite stable, but not so strong that it slows the overall reduction to methanol.

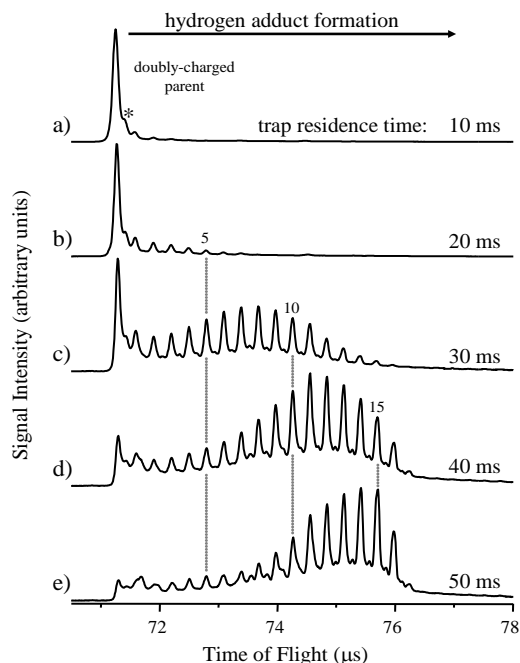


**Fig. 3.** Probing the formation of the carbamate ion from the reaction of pyridine with negatively charged CO<sub>2</sub> clusters using vibrational spectroscopy. The vibrational band highlighted in red indicates the appearance of the C-N stretching transition associated with formation of the covalent bond to the CO<sub>2</sub> group.

It is useful to note that in a classic case of serendipity, we have also carried out an extensive study of the anomalously large solvatochromic response of the C-H stretching mode in the formate ion,  $\text{HCO}_2^-$  ( $2456\text{ cm}^{-1}$  in bare formate vs.  $2803\text{ cm}^{-1}$  in aqueous solution). This is particularly relevant to  $\text{CO}_2$  reduction since the  $\text{H}^- + \text{CO}_2$  asymptote is formally the reaction coordinate for reductive activation. That study was carried out under DOE support for the purpose of characterizing excess electron-induced proton transfer in the formic acid dimer. The strong solvent-dependence of the C-H stretch was traced to a dramatic dependence of the electronic wavefunction as the C-H bond is broken. Like the situation in NaCl, formate exhibits rapid internal charge-transfer as the  $\text{H-CO}_2^-$  configuration of the ion dissociates into  $\text{H}^- + \text{CO}_2$  products. Although not acknowledged in our papers directly under AFOSR support, the relevance to our work on  $\text{CO}_2$  activation illustrates the synergies at play in seemingly disparate projects.

### II.C. Development of cryogenic ion chemistry to study microsolvated condensed phase ions using tagging

Prior to this grant period, the scope of our program was limited to chemical species that can be produced in ionized free jet expansions where, for small systems, the expansion itself can quench the internal energy enough to generate Ar-tagged species. As such, this approach could only be used on volatile species. To expand the range of systems accessible with “messenger” spectroscopies, we integrated an electrospray ionization source into the TOF spectrometer with a cryogenically cooled ion trap as indicated in Fig. 1. Our approach is a variation of that first demonstrated by Wang *et al.* and efficiently cools a broad range of chemical species (e.g. organometallics, polypeptides, carbohydrates, etc.) through collisions with He buffer gas in a  $\sim 10\text{ K}$  quadrupole ion trap. A variety of rare gas or small molecule tags (e.g.  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{N}_2$ , Ar,



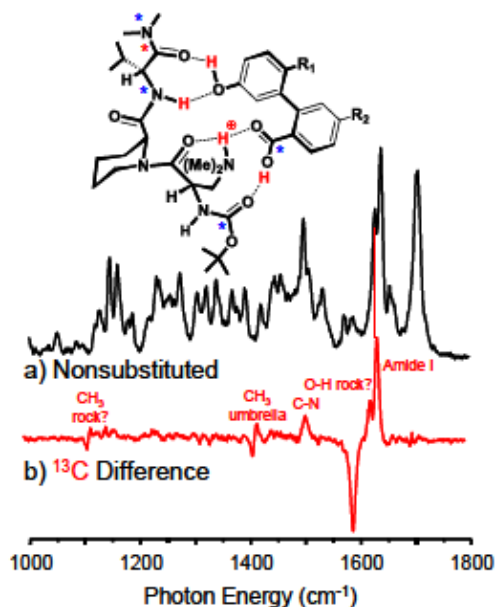
**Fig. 4.** Mass spectra demonstrating the effect of trap residence time on  $\text{H}_2$  tagging efficiency. The doubly charged parent ion ( $\text{OOC}(\text{CH}_2)_{10}\text{COO}^-$ ) is observed to accumulate increasing numbers of  $\text{H}_2$  molecules as the residence time is lengthened from (a) 10 ms to (e) 50 ms. The asterisk in (a) indicates natural  $^{13}\text{C}$  abundance.



etc.) can then be condensed onto the ion of interest by adding any of these to the buffer gas mixture and adjusting the trap temperature. This is demonstrated with  $\text{H}_2$  for the doubly charged anion of dodecanedioic acid in Fig. 4, where increasing the trap residence time is shown to increase the number of  $\text{H}_2$  molecules on the anion. This capability was reported in ref. [5], introduced with AFOSR support, has enabled us to rapidly engage catalytic systems currently being optimized by our synthetic colleagues.

### IID. Structure of the catalyst-substrate complex for stereoselective bromination based on a biomimetic host-guest approach

Catalytic bromination of aryl compounds provided an ideal context in which to follow the multidentate linkages that selectively bind a substrate (S) to a peptidic catalyst (C), with the resulting structure indicated at the top of Fig. 5. That study has just been published in *Science*, in ref. [8], again along with a *Perspective*, and represents a collaborative effort between our group and Scott Miller's synthesis team at Yale, along with theoretical support from Anne McCoy (Ohio State). Structural analysis was achieved through extensive use of site-specific isotope labeling as well as IR-IR double resonance, where the lower trace in Fig. 5 presents a typical difference spectrum highlighting the fact that only a few bands are significantly affected when  $^{13}\text{C}$  is placed in the acid group on the biaryl substrate.

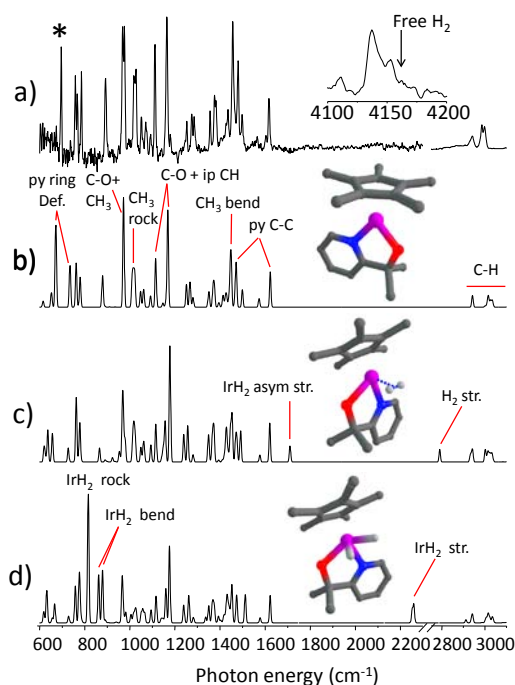


**Fig. 5.** Schematic structure of the catalyst-substrate (C-S) docked species (top center) and the vibrational predissociation spectrum of a) the unlabeled (all  $^{12}\text{C}$ ) catalyst-substrate species and b), the difference spectrum resulting from incorporation of a single  $^{13}\text{C}$  atom into the acid functionality (highlighted in red).

The ability to pinpoint transitions arising from particular oscillators (or group of oscillators) embedded within complex structures will be crucial as we interrogate increasingly large organometallic catalysts. The use of isotopic substitution enables identification of not only the fingerprint of the ligand functionalities through selective incorporation of  $^{13}\text{C}$  and  $^{15}\text{N}$ , but can also isolate transitions associated with active intermediates like metal-O bonds through  $^{18}\text{O}$  substitution.

### III. Characterization of an organometallic water splitting catalyst with cold ion vibrational spectroscopy

Consistent with the main goal of applying the cryogenic methodology to water splitting catalysts, we also obtained the vibrational predissociation spectra of two related organometallic, half-sandwich iridium species which have been recently reported as activated intermediates in the context of homogenous water oxidation. The resulting spectra display very sharp ( $\sim 5\text{ cm}^{-1}$ ), well-resolved bands as illustrated in Fig. 6, and as such, provide a stringent test for electronic structure calculations. The observed bands are accurately recovered by harmonic predictions. The spectra also reveal subtle distortions of the ligand structure when a solvent molecule (acetonitrile) is directly coordinated with the metal center. These results were reported in ref. [11]. At the very end of this grand period, we also obtained a spectrum of molecular oxygen coordinated to a Mn atom in another oxidation catalyst, and a manuscript (ref. [13]) describing that work has been submitted for publication.



**Fig. 6:** a)  $\text{H}_2$  predissociation spectrum of  $1 \cdot 2\text{H}_2$  and b-d) calculated (cam-B3LYP/SDD/6-311++G(d,p) level) structures and harmonic spectra of b) bare **1**, c) **1**( $\text{H}_2$ ) and d) **1** $\text{H}_2$ .

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## **Graduate Students supported by this grant**

Rachael Relph  
Mike Kamrath  
Arron Wolk  
Christopher Leavitt

## **Postdoctoral Associates supported by this grant**

Rachael Relph

## **Inventions and patent disclosures**

One patent disclosure has been issued based on the work supported by this grant.: International Application PCT/US11/55681, “Use of Cryogenic Ion Chemistry to Add a Structural Characterization Capability to Mass Spectrometry Through Linear Action Spectroscopy

## **Honors and Awards during grant period**

2012 Alexander von Humboldt Senior Research Award  
2009 American Academy of Arts and Sciences

## **Invited Lectures during grant period**

(2009)

Watkins Prize Lectures, Wichita State University (2)  
ACS National Meeting invited lecture (Washington, DC)  
APS March Meeting invited lecture (Pittsburgh)  
Holy Cross University, Department Colloquium  
Northwestern, Department Colloquium  
University of Texas, Physical Chemistry seminar  
ASMS National meeting, Philadelphia, invited lecture  
ASMS workshop on ion spectroscopy, Asilomar (invited lecture)  
Workshop on cold ion traps, Aarhus Denmark (Invited lecture)  
Session Chair, Gordon Conf. on Molecular Energy Transfer  
Session Chair, Gordon Conf. on Biological Molecules in the Gas Phase

(2010)

GRC on Photoions  
“Spectroscopy of Real Systems,” Kyoto Japan  
ACS National meeting, San Francisco (Floppy molecules)  
ACS National meeting, Boston (Hydrates)  
AFOSR Contractors Meeting  
Columbus mini-symposium on floppy molecules  
GRC on Water  
GRC on Atomic and Molecular Interactions  
GRC Molecular and Ionic Clusters  
Site visit for CCI “Fueling the Future” overview talk  
Pacifichem (2 talks, Frontiers in state-to-state dynamics and Clusters )

## MIT Frontiers in Optics Lecture

### (2011)

1. UT Austin
2. Johns Hopkins
3. Brown
4. Washington University St. Louis
5. Inaugural John B. Fenn Memorial Lecture, Virginia Commonwealth University
6. ACS Anaheim- Spectroscopy of Isolated Biopolymers
7. Telluride workshop on vibrational spectroscopy of complex systems
8. Size-selected clusters – Davos, Switzerland
9. Argonne National Laboratory Chemistry Division Seminar
10. Dynamics of Molecular Collisions, Snowbird, Utah
11. Air Force Office of Scientific Research, Contractor's meeting, Pasadena, California
12. Department of Energy, CPIMS Contractor's meeting, Baltimore, Maryland
13. Conference on Molecular Energy Transfer, Oxford, England
14. Science Saturday's "The Wild World of Electrified Water!", Yale University

### (2012)

1. Basler Gesellschaft Lecture
  2. Spectroscopy Frontier Lectures (3) Ohio State
  3. FOR618 Symposium, Bochum, Germany
  4. Baker Lecture Symposium, Cornell
  5. ACS National Meeting, San Diego
  6. Biomolecules in the gas phase, Les Diablerets, Switzerland
  7. Physical Chemistry Seminar: U. Florida, Gainesville
  8. Physical Chemistry Seminar, U. Pennsylvania
  9. Keynote Lecture, Vibrational Spectroscopy GRC
  10. Department Seminar, Bridgewater State University, MA
- Discussion Leader:
11. Molecular and Ionic Clusters GRC, Ventura ,CA
  12. Photoions GRC, Galveston, Texas